## **ORGANOMETALLICS**

# Photocatalytic Aerobic Thiol Oxidation with a Self-Sensitized Tellurorhodamine Chromophore

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**Supporting Information** 

**ABSTRACT:** Aerobic oxidation of thiols to disulfides was achieved photocatalytically using a tellurorhodamine chromophore (9-mesityl-3,6-bis(dimethylamino)telluroxanthylium hexafluorophosphate) as both the sensitizer and catalyst. The proposed mechanism, supported experimentally and computationally with DFT, involves the formation of a tellurorhodamine telluroxide from reaction with water and singlet oxygen generated by irradiation of the tellurorhodamine. The oxidation to the telluroxide is accompanied by the formation of hydrogen peroxide. The telluroxide oxidizes thiols to regenerate the tellurorhodamine and the disulfide plus water. Mechanistically, DFT suggests adding two thiols to the



telluroxide with the loss of  $H_2O$  to give a trigonal-bipyramidal Te(IV), which undergoes concerted loss of disulfide to regenerate 1. Oxidation of thiophenol and 2-naphthalenethiol was complete after 2 h of irradiation with visible light under atmospheric conditions. Oxidation of the electron-poor 2,6-dichlorothiophenol, the sterically bulky *tert*-butylmercaptan, and aliphatic dodecanethiol was slower. The two aliphatic thiols displayed competing catalyst degradation. The corresponding selenorhodamine chromophore (9-mesityl-3,6-bis(dimethylamino)selenoxanthylium hexafluorophosphate) does not form the corresponding selenoxide under similar conditions and photooxidizes thiophenol and 2-naphthalenethiol much more slowly ( $\leq 6\%$  conversion after 2–3 h).

#### INTRODUCTION

Homogeneous metal-catalyzed aerobic oxidation is a widely used method for small-molecule transformations but often is restricted by the stoichiometric use of heavy-metal cooxidants.<sup>1</sup> The use of photoinduced redox catalysis for such transformations has increased in recent years due to its potential for the green production of small molecules at both the laboratory and industrial scale.<sup>2–4</sup> Photocatalysts such as TiO<sub>2</sub> that utilize atmospheric oxygen as an oxidant are only active in the UV region, which drastically reduces their light absorption efficiency.<sup>5</sup> Organic dyes have been developed as photoredox catalysts for a variety of transformations, including the oxidation of thiols to disulfides,<sup>6</sup> anti-Markovnikov additions to alkenes,<sup>7,8</sup> and oxidation of amines to iminium salts.<sup>9</sup>

Chalcogenorhodamine dyes such as those shown in Scheme 1 are similar in structure to the rhodamine, oxazine, thiazine, and azine dyes that have been used as visible-light-driven photocatalysts in reactions that use singlet oxygen  $({}^{1}O_{2})$  as an oxidant.<sup>10</sup> While both seleno- and tellurorhodamines generate  ${}^{1}O_{2}$  efficiently upon irradiation, tellurorhodamines undergo photooxidation to telluroxides, while selenorhodamines do not undergo oxidation to the corresponding selenoxide.<sup>11,12</sup>

Organotellurium compounds have been used as redox auxiliaries with a porphyrin photosensitizer for photocatalytic

aerobic thiol oxidation.<sup>6</sup> Organotellurium compounds have also been used as catalysts for the oxidation of thiols to disulfides with  $H_2O_2$ .<sup>13–16</sup> The proposed active oxidant in these systems is a telluroxide—a Te(IV) compound—that is reduced back to the corresponding telluride—a Te(II) compound—during thiol oxidation. Glutathione has been used as a stoichiometric reducing agent for telluroxides formed either by  $^1O_2$  oxidation<sup>11,12</sup> or by hypochlorite oxidation<sup>17</sup> of tellurium-containing chromophores. Telluroxides have also been shown to oxidize a variety of substrates without the addition of cooxidants.<sup>18</sup>

As an oxidant,  ${}^{1}O_{2}$  is advantageous, both economically and environmentally. However, a short lifetime, limited scope, and lack of selectivity hinder the use of  ${}^{1}O_{2}$  for many aerobic oxidation reactions.<sup>19</sup> The ease of  ${}^{1}O_{2}$  oxidation of tellurides to telluroxides, which can then be used as a chemical oxidant, can be extended to tellurium chromophores, which self-sensitize the

Received: March 6, 2017

Special Issue: Tailoring the Optoelectronic Properties of Organometallic Compounds with Main Group Elements

Scheme 1. Oxidation of Tellurorhodamine 1 to Tellurorhodamine Telluroxide 2 with  ${}^{1}O_{2}$  and Water and the Structure of Selenorhodamine 3



production of  ${}^{1}O_{2}$  to produce catalytic systems requiring only atmospheric  $O_{2}$ , water and visible light irradiation.

Herein, we report the use of tellurorhodamine 1 (Scheme 1) as a visible-light-active photocatalyst for the selective aerobic oxidation of thiols to disulfides under ambient temperature and pressure in air according to eq 1. The role of telluroxide 2 (Scheme 1) as the active form of the catalyst and other Te(IV) intermediates is described. The performance of 1 as a photocatalyst is contrasted with the performance of selenorhod-amine 3, which does not form the corresponding selenoxide intermediate. We provide a detailed mechanism for the photooxidation reaction based on experimental results and DFT calculations.

$$2RSH + 1/2O_2 \xrightarrow[light]{\text{catalyst}} RSSR + H_2O$$
(1)

#### RESULTS AND DISCUSSION

Synthesis of Chalcogenorhodamine Dyes 1 and 3. The chalcogenorhodamines 1 and 3 were prepared by addition of the Grignard reagent prepared from 2-bromomesitylene to the corresponding chalcogenoxanthone 4 or 5 (Scheme 2).<sup>11,20</sup>

### Scheme 2. Synthesis of Tellurorhodamine 1 and Selenorhodamine 3



Following addition of the Grignard reagent, the reaction mixtures were stirred for 24 h and were then poured into 10% aqueous HPF<sub>6</sub> to precipitate the dyes, which were isolated in 80% yield for 1 and 62% yield for 3.

Photophysical Properties of Chalcogenorhodamine Dyes 1 and 3. Tellurorhodamine 1 absorbs light with  $\lambda_{max}$  of 600 nm in MeOH ( $\varepsilon = 8.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), and selenorhodamine 3 absorbs light with  $\lambda_{max}$  of 568 nm in MeOH ( $\varepsilon = 1.03 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ). The quantum yield for <sup>1</sup>O<sub>2</sub> generation ( $\Phi(^{1}O_{2})$ ) for 1 is 0.75  $\pm$  0.03,<sup>11</sup> and  $\Phi(^{1}O_{2})$  for selenorhodamine 3 is 0.85  $\pm$  0.03, as determined by timeresolved spectroscopy of <sup>1</sup>O<sub>2</sub> phosphorescence.<sup>12</sup>

Values of  $\Phi({}^{1}O_{2})$  are related to quantum yields for triplet generation ( $\Phi_{T}$ ) and, strictly on the basis of spin-orbit effects, the value of  $\Phi_{T}$  for 1 containing the heavier Te atom (filled 4d shell) would be expected to be greater than that of 3 containing the lighter Se atom (filled 3d shell).<sup>21</sup> However, the lifetime of the triplet state ( $\tau_{\rm T}$ ) for Te-containing chromophores is shorter than  $\tau_{\rm T}$  for comparable Se-containing dyes and relaxation of the triplet by pathways other than quenching with oxygen becomes competitive (i.e., phosphorescence) in air-saturated solutions.<sup>22</sup> The fraction of triplets producing  ${}^{1}O_{2}$  can be reduced as triplet lifetimes become shorter, and the smaller value of  $\Phi({}^{1}O_{2})$  for **1** relative to **3** is certainly consistent with this analysis.

**Oxidation with H\_2O\_2.** In earlier work, we examined a number of tellurides (Chart 1) as catalysts for the activation of

Chart 1. Diorganotelluride Catalysts for the Activation of  $\rm H_2O_2$ 



 $H_2O_2$  for the oxidation of thiols to disulfides, with the corresponding telluroxide being the active form of the catalyst.<sup>15,16</sup> Rate constants for oxidation of the tellurides to the telluroxides with  $H_2O_2$ ,  $k_{H_2O_2}$ , are 2  $M^{-1}$  s<sup>-1</sup> for telluropyrylium compound  $6^{22}$  and 3.6–28  $M^{-1}$  s<sup>-1</sup> for neutral diorganotellurides 7–9.<sup>16</sup> We had thought that tellurorhod-amine 1 would be an excellent candidate as a catalyst for the oxidation of thiols to disulfides with  $H_2O_2$ : 1 is oxidized to telluroxide 2 with  $H_2O_2$ , 2 is reduced by glutathione to return 1, and the 9-mesityl group protects both the reduced and oxidized forms.<sup>11</sup> However, as described below,  $k_{H_2O_2}$  for oxidation of 1 to 2 is orders of magnitude smaller than  $k_{H_2O_2}$  for the diorganotellurides of Chart 1.

The oxidation of 1 (1 × 10<sup>-5</sup> M) to 2 with H<sub>2</sub>O<sub>2</sub> in 10% H<sub>2</sub>O/90% MeOH at 293 K was followed by UV-vis spectroscopy, as shown in Figure 1. Reaction with 0.05 M H<sub>2</sub>O<sub>2</sub> was complete after 4800 s, and telluroxide 2 was identified as the product of oxidation (Figure 1a).<sup>11</sup> The rate of appearance of 2 was followed at 680 nm as a function of time for three concentrations of H<sub>2</sub>O<sub>2</sub> (0.01, 0.03, and 0.05 M). Typical first-order rate plots of the data for the three H<sub>2</sub>O<sub>2</sub> concentrations are shown in Figure 1b. A plot of the pseudo-first-order rate constants as a function of 1 with H<sub>2</sub>O<sub>2</sub>,  $k_{\rm H_2O_2}$  in 90% aqueous MeOH at 293 K is  $(1.1 \pm 0.01) \times 10^{-2} \, {\rm M}^{-1} \, {\rm s}^{-1}$ ,



**Figure 1.** Oxidation of a  $1 \times 10^{-5}$  M solution of 1 with H<sub>2</sub>O<sub>2</sub> in 10% H<sub>2</sub>O/90% MeOH to give telluroxide 2 at 293 K: (a) spectral changes for the conversion of 1 to 2 with 0.05 M H<sub>2</sub>O<sub>2</sub>; (b) typical first-order rate plots for the appearance of 2 monitored at 680 nm at 0.01, 0.03, and 0.05 M H<sub>2</sub>O<sub>2</sub>; (c) plot of mean pseudo-first-order rate constants from triplicate runs as a function of H<sub>2</sub>O<sub>2</sub> concentration. Error bars represent ±1 standard deviation.

which is 180-fold smaller than  $k_{\rm H_2O_2}$  for **6** and 2500-fold smaller than  $k_{\rm H_2O_2}$  for **7** under similar conditions. For comparison, selenorhodamine **3** does not react with 0.05 M H<sub>2</sub>O<sub>2</sub> over a 2 h time period.

Photochemical Reactivity of Chalcogenorhodamine Dyes 1 and 3. Solutions of either 1 or 3  $(1 \times 10^{-5} \text{ M})$  in degassed solutions of MeOH or CDCl<sub>3</sub> under a N<sub>2</sub> atmosphere showed less than 5% bleaching upon irradiation with white LEDs (24 W, LED spectrum in Figure S1 in the Supporting Information) over a 2 h time period. Irradiation of a  $1 \times 10^{-5}$  M solution of 1 in air-saturated 10% H<sub>2</sub>O/90% MeOH with the white LEDs gave photooxidation to telluroxide 2 ( $\lambda_{max}$  664 nm) over an 18 min period with an isosbestic point at 616 nm (Figure 2a). In contrast, no loss of the chromophore of 3 in air-saturated 10% H<sub>2</sub>O/90% MeOH was observed with irradiation with the white LEDs over a 2 h time period.

Irradiation of a  $1 \times 10^{-5}$  M solution of 1 in air-saturated dry CDCl<sub>3</sub> gave a different outcome. After 30 s of irradiation, the appearance of 2 at 650 nm was observed, but 2 was not stable to the conditions of the reaction. The ability of the telluroxide O atom in tellurorhodamine telluroxides to act as an inter- or intramolecular nucleophile has been described.<sup>11</sup> The addition of 2.5% water to the CDCl<sub>3</sub> solution prior to irradiation increased the stability of 2, and photooxidation of 1 to 2 was observed with an isosbestic point at 600 nm (Figure 2b).

**Photocatalytic Thiol Oxidation.** Photocatalytic oxidations of aliphatic and aromatic thiols to disulfides were monitored by <sup>1</sup>H NMR spectroscopy using CDCl<sub>3</sub> containing 2.5% H<sub>2</sub>O by volume as solvent and 1 mol % of tellurorhodamine 1 or selenorhodamine 3 (relative to thiol) as the photocatalyst. The reaction mixtures were irradiated with white LEDs under ambient conditions. The results are summarized in Table 1. Thiophenol and 2-naphthalenethiol were completely oxidized to disulfides (Table 1, entries 1 and 3, respectively) within 2 h, as shown in Figure 3 for oxidation of 2-naphthalenethiol.



Figure 2. Photooxidation of a  $1 \times 10^{-5}$  M solution of 1 to give telluroxide 2 irradiated with 24 W white LEDs (a) in 10% H<sub>2</sub>O/90% MeOH (spectrum taken every 2 min for 18 min) and (b) in air-saturated CDCl<sub>3</sub> containing 2.5% water (spectrum taken every 2 min for 16 min).

Table 1. Oxidation of Aromatic and Aliphatic Thiols (5  $\times$  10<sup>-2</sup> M) to Disulfides with 1 mol % of 1 or 3 (5  $\times$  10<sup>-4</sup> M) under Aerobic Conditions in 2.5% H<sub>2</sub>O/CDCl<sub>3</sub>

| entry          | photocatalyst | thiol                  | irradiation<br>time (h) | disulfide<br>conversion<br>(%) <sup>a</sup> |
|----------------|---------------|------------------------|-------------------------|---|
| 1              | 1             | thiophenol             | 2                       | ≥99   |
| 2              | 3             | thiophenol             | 3                       | 5   |
| 3              | 1             | 2-naphthalenethiol     | 2                       | ≥99   |
| 4              | 3             | 2-naphthalenethiol     | 2                       | 6   |
| 5              | 1             | 2,6-dichlorothiophenol | 2                       | 52  |
| 6 <sup>b</sup> | 1             | tert-butylmercaptan    | 2                       | 38  |
| 7 <sup>6</sup> | 1             | 1-dodecanethiol        | 2                       | 25  |
| an .           |               | but by                 | <i>C</i> <b>-</b>       | 1 1.1                                       |

<sup>*a*</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>*b*</sup>Loss of **1** was observed with time.

Oxidation was selective, as no other products were apparent upon completion of reaction.

The completion of thiol oxidation was indicated by a colorimetric change in the appearance of the reaction mixture. The persistence of 2—i.e., 2 no longer being reduced to 1—was visually identifiable by the bathochromic absorbance shift resulting in a change from a blue to a green solution (Figure S2 in the Supporting Information). After complete conversion of thiol to disulfide, the addition of more thiol resulted in the immediate reduction of 2 to 1 and further thiol oxidation was observed with continued irradiation with visible light.



**Figure 3.** <sup>1</sup>H NMR spectra following the photooxidation of 2naphthalenethiol with 1 mol % of 1 under visible light irradiation in  $CDCl_3$  containing 2.5% water at 0, 1, and 2 h. The thiol proton signal at 3.5 ppm was used to monitor reaction progress.

As described above, irradiation of degassed solutions of 1 under a  $N_2$  atmosphere in either CDCl<sub>3</sub> or MeOH did not give 2. Similarly, irradiation of degassed solutions of 1 and thiophenol did not give diphenyl disulfide. These data are consistent with  $O_2$  being an integral component of the photocatalysis.

Using selenorhodamine **3** as the photocatalyst with thiophenol (Table 1, entry 2) and 2-naphthalenethiol (Table 1, entry 4) resulted in conversions to disulfide of  $\leq 6\%$  after 2–3 h of irradiation. The observed conversion is likely the result of thiol oxidation by  ${}^{1}O_{2}$  produced during irradiation rather than **3** acting as a photocatalyst. No color change and no loss of absorbance of **3** were observed by UV–vis absorption spectroscopy during irradiation, indicating that **3** was not lost during the reaction and does not produce observable amounts of selenoxide. Similarly, irradiation of degassed solutions of **3** and thiophenol did not give diphenyl disulfide.

Oxidation of 2,6-dichlorothiophenol was slower than the oxidation of either thiophenol or 2-naphthalenethiol, as nearly half of the initial thiol concentration remained after 2 h (Table 1, entry 5). Catalyst degradation was not observed by comparing the absorbance of 1 before and after irradiation for 2 h. Oxidation of *tert*-butyl mercaptan was slower still with 38% conversion after 2 h (Table 1, entry 6). Oxidation of the aliphatic 1-dodecanethiol gave only 25% oxidation after 2 h

(Table 1, entry 7). Oxidation of both *tert*-butyl mercaptan and 1-dodecanethiol gave significant catalyst degradation after 2 h of irradiation, as observed spectrophotometrically by loss of the chromophore of 1.

**Thiol Reduction of Telluroxide 2.** The reduction of 2 to 1 was examined by stopped-flow spectroscopy using thiophenol, 2-naphthalenethiol, 2,6-dichlorothiophenol, and 1-dodecanethiol as reductants. A solution of 2 ( $5 \times 10^{-6}$  M) for the stopped-flow studies was prepared by dissolving 1 in 10% water/90% MeOH and photooxidizing the solution to produce 2.

The rates of reduction of **2** using 100 equiv of thiol ( $5 \times 10^{-4}$  M) were followed by stopped-flow spectroscopy monitoring the change in absorbance of **2** at 655 nm as shown in Figure 4. 2-Naphthalenethiol, thiophenol, and 2,6-dichlorothiophenol gave pseudo-first-order rate constants of 1.46 ± 0.08, 1.06 ± 0.06, and 0.808 ± 0.007 s<sup>-1</sup>, respectively.

If the pseudo-first-order rate constants are divided by the thiol concentration (5 × 10<sup>-4</sup> M), approximate second-order rate constants for 2-naphthalenethiol, thiophenol, and 2,6-dichlorothiophenol are calculated to be 2.9 × 10<sup>3</sup>, 2.1 × 10<sup>3</sup>, and 1.6 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively. Initial rates for the oxidation of thiophenol to diphenyl disulfide with H<sub>2</sub>O<sub>2</sub> in aqueous MeOH have been reported.<sup>23</sup> On the basis of an initial rate of (1.5 ± 0.4) × 10<sup>-7</sup> M<sup>-1</sup>min<sup>-1</sup> for the appearance of diphenyl disulfide with 1.0 × 10<sup>-3</sup> M thiophenol and 3.75 × 10<sup>-3</sup> M H<sub>2</sub>O<sub>2</sub>, a second-order rate constant of (6.7 ± 1.7) × 10<sup>-4</sup> M<sup>-1</sup> s<sup>-1</sup> can be calculated. The rate constant for thiophenol oxidation with H<sub>2</sub>O<sub>2</sub> produced during the reaction would not contribute significantly to thiol oxidation.

The slower rate of reduction of 2 with 2,6-dichlorothiophenol is consistent with the 52% yield of disulfide after 2 h (Table 1, entry 4). The slower rate of reduction is likely a result of the electron-withdrawing chlorine groups decreasing the nucleophilicity of the thiol S atom.

A solution of **2** was titrated with thiophenol, 2naphthalenethiol, or 2,6-dichlorothiophenol in order to determine the number of molar equivalents of thiol required for complete conversion back to **1**. Two molar equivalents of aromatic thiol proved sufficient for complete reduction of **2** to



Figure 4. Reduction of 2 to 1 as monitored by stopped-flow spectroscopy from the diminishing of the telluroxide peak at 655 nm under pseudo-firstorder conditions (a) by 2,6-dichlorothiophenol (green squares), thiophenol (red diamonds), and 2-naphthalenethiol (blue triangles); (b) by 1dodecanethiol.

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1, as determined by UV-vis spectroscopy (Figures S3-S5 in the Supporting Information).

In contrast to reactions with the aromatic thiols, reduction of **2** using excess 1-dodecanethiol under pseudo-first-order conditions did not result in a first-order loss of **2** (Figure 3b), which is indicative of a competing reaction. X-ray crystal structures in earlier studies documented intramolecular and bimolecular addition of nucleophiles to the 9-position of the tellurorhodamine telluroxides, which disrupts the cyanine-like chromophore.<sup>11</sup> Similar chemistry with 1-dodecanethiol would lead to loss of catalyst. Although the 9-mesityl group sterically protected telluroxide **2** from nucleophilic addition to the 9-position during reductions with 2 equiv of glutathione,<sup>11</sup> addition of an excess of 1-dodecanethiol to telluroxide **2** appears to be competitive with reduction of **2** to **1**.

**Mechanism of Photooxidation of 1 to 2.** Once formed, telluroxide **2** is an excellent oxidizing agent for converting thiols to disulfides. The mechanism of photooxidation of **1** to **2** was examined both computationally and experimentally. The data are consistent with the general mechanism proposed in Scheme 3 for oxidation of diorganotellurides to telluroxides. The initial

Scheme 3. Proposed Mechanism of Telluride Oxidations with  ${}^{1}O_{2}$  in the Photooxidation of 1 to  $2^{a}$ 



<sup>*a*</sup>The inset shows the structure of the hydroxyl(perhydroxy)selenane **D**.

formation of the pertelluroxide intermediate A of Scheme 3 has been proposed as the starting point for addition of  ${}^{1}O_{2}$  to diorganotellurides.<sup>22,24</sup> The pertelluroxide A can oxidize a second diorganotelluride (i.e., a second molecule of 1), leading to reduction of A to the telluroxide (i.e., 2) and oxidation of the diorganotelluride to the telluroxide (i.e., 2).<sup>22,24</sup> The stoichiometry of this chemistry was established in flash photolysis studies of telluropyrylium dye 6 in MeOH (Chart 1).<sup>22</sup> The reversible addition of H<sub>2</sub>O to the diorganotelluroxide B forms the (dihydroxy)tellurane C.<sup>22,25</sup>

Irradiation of 1 in the presence of water facilitated telluroxide formation. Photooxidation of  $1.0 \times 10^{-5}$  M 1 to 2 in 10% H<sub>2</sub>O/ 90% MeOH also produced ( $8.4 \pm 0.6$ ) ×  $10^{-6}$  M H<sub>2</sub>O<sub>2</sub>. Concentrations of H<sub>2</sub>O<sub>2</sub> were measured by an established spectrophotometric technique using oxo[5,10,15,20-tetrakis(4pyridyl)porphyrinato]titanium(IV).<sup>26</sup> The approximately 1 equiv of H<sub>2</sub>O<sub>2</sub> produced upon photooxidation of 1 to 2 in the presence of H<sub>2</sub>O suggests that oxidation of 1 to 2 via the pertelluroxide A is less important in the presence of water.

The addition of water to pertelluroxide **A** would form the hydroxy(perhydroxy)tellurane **B**. We were unable to observe the hydroxy(perhydroxy)tellurane analogue of telluroxide **2** by <sup>125</sup>Te NMR ( $\delta$  883 for the <sup>125</sup>Te signal of **2**).<sup>11</sup> However, the addition of H<sub>2</sub>O<sub>2</sub> to selenoxides gives the hydroxy-(perhydroxy)selenane **D** (the selenium analogue of **B**, Scheme

3). Selenanes **D** are viable intermediates and have been observed by mass spectrometry and <sup>77</sup>Se NMR spectroscopy.<sup>27</sup> Loss of  $H_2O_2$  from the hydroxy(perhydroxy)tellurane **B** forms the telluroxide. The intermediates shown in Scheme 3 with tellurorhodamine 1 have been studied by DFT, as discussed below.

While  $H_2O_2$  is produced upon photooxidation of 1 to 2 in the presence of H<sub>2</sub>O, one can ask whether the presence of the thiol influences the production of  $H_2O_2$ . A solution of 1 (5  $\times$  $10^{-4}$  M) and thiophenol (5 ×  $10^{-2}$  M) in chloroform and water (2.5% by volume) was irradiated with the white LEDs. Upon a visual change in color, from a blue to a green solution, water was added to create a biphasic solution and the concentration of  $H_2O_2$  in the aqueous layer was determined to be  $(1.8 \pm 0.1)$  $\times$  10<sup>-4</sup> M using oxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato titanium(IV) as described above,<sup>26</sup> which corresponds to roughly 0.4 equiv of  $H_2O_2$  relative to 1. On the basis of the rates of oxidation of 1 and thiophenol described above with  $H_2O_2$ , the  $H_2O_2$  produced during the photocatalysis does not compete as an oxidant with 2 for the oxidation of thiophenol to the disulfide or with  ${}^{1}O_{2}$  for the oxidation of 1 to 2.

**DFT Calculations.** Structural optimizations were performed with Gaussian 09 software<sup>28</sup> at the B3LYP level<sup>29–31</sup> using 6-31+G(d) (C, O, S, N, H atoms)<sup>32–34</sup> and LanL2DZ (Te atoms)<sup>35–37</sup> split basis sets.<sup>38</sup> The HOMO and LUMO molecular orbital maps of the reduced and oxidized mesityl-substituted tellurorhodamine **1** are shown in Figure 5.



Figure 5. Frontier molecular orbitals (FMOs) from the DFT optimized geometries of the reduced tellurorhodamine 1 and oxidized 2 of the (a) LUMO and (b) HOMO of 1 and the (c) LUMO and (d) HOMO of 2.

The HOMOs of both the reduced species 1 and oxidized species 2 are located primarily on the N and C atoms of the 3,6-diaminoxanthylium core with minimal contributions from the Te atoms (Figure 5b,d). The LUMO of the reduced species 1 has a major contribution from the Te atom (Figure 5a), which is absent in the LUMO of telluroxide 2. Furthermore, the LUMO of the oxidized species 2 has a major contribution from the C atom in the 9-position within the xanthylium core, which supports the addition of a nucleophile at this position to give tellurorhodamine degradation products postulated for reactions with aliphatic thiols.

**Oxidation of 1 to 2.** Reaction energy diagrams of oxidation and reduction of the telluride complex were determined using

the calculated Gibb's free energies  $(\Delta G)$  according to the equation

$$\Delta G = \left[\sum E_{\text{prod}}\right] - \left[\sum E_{\text{reac}}\right]$$

The energy diagram of the reaction of 1 with  ${}^{1}O_{2}$  to form 2 is shown in Figure 6. The total  $\Delta G$  of oxidation of 1 to 2 with  ${}^{1}O_{2}$ 



Figure 6. Reaction energy diagram of the formation of 2 from the reaction of 1 with  ${}^{1}\mathrm{O}_{2}$  and  $H_{2}\mathrm{O}.$ 

was calculated to be 12.7 kcal/mol. Initial coordination of  ${}^{1}O_{2}$  to the Te(II) of 1 to give pertelluroxide A (see also Scheme 3) is slightly uphill in energy (1.17 kcal/mol). Coordination of H<sub>2</sub>O followed by a proton shift forms the hydroxy-(perhydroxy)tellurane B as a Te(IV) intermediate (see also Scheme 3). Previous to this study, the role of H<sub>2</sub>O in the oxidation mechanism was not well understood. The oxidation of 1 occurred slowly in anhydrous solvent and H<sub>2</sub>O addition allowed the reaction to proceed at a faster rate. We propose this specific water-coordination mechanism as a plausible explanation for the latter. The final step in the formation of 2 is elimination of H<sub>2</sub>O<sub>2</sub> ( $\Delta G = -18.5$  kcal/mol), which supports the experimentally observed results.

Thiol Reduction of 2 to 1. To simplify the calculations, the reduction of 2 with a thiol to give 1 was calculated using methanethiol, which upon oxidation gives dimethyl disulfide. The  $\Delta G$  value of the reduction of 2 to 1 and subsequent disulfide formation was calculated to be -46.6 kcal/mol. The computationally examined structures in Figure 7 were based on previously hypothesized substitution reactions, which involved a (dihydroxy)tellurane intermediate (C in Scheme 3).<sup>15,16</sup> There is a slight downhill transition from telluroxide 2 to the (dihydroxy)tellurane C ( $\Delta G = -0.45$  kcal/mol) in Figure 7, which is consistent with an equilibrium involving telluroxide 2 and  $H_2O$ .<sup>22,25</sup> Substitution of each of the hydroxy ligands with methanethiol (generating water) and subsequent reductive elimination of dimethyl disulfide re-forms 1, which supports the 2:1 thiol to telluroxide ratio for telluroxide reduction that was observed experimentally.

Intermediate E, in which the Te(IV) center has two methanethiolate ligands, conceptually can undergo reductive elimination via a stepwise process<sup>15,16</sup> or via a concerted reductive elimination, which is supported by the DFT calculations.<sup>39</sup> The transition state for the reductive elimination (TS<sub>E</sub>) from E to 1 is 26 kcal/mol higher than intermediate E and shows shortening of the S–S bond by a decrease in the S–Te–S bond angle.

The inset of Figure 7 shows the changes in geometry around the Te center in going from intermediate E (inset left) to transition state  $\mathbf{TS}_{E}$  (inset center) to 1 (inset right). The Te(IV) center of E has trigonal-bipyramidal geometry with the axial thiolate ligands distorted from linearity by the equatorial lone pair of electrons. As E progresses toward the transition state, the geometry around Te changes from trigonal bipyramidal to something approaching square pyramidal: the two Te–C bonds, one elongated Te–S bond (from 2.69 to3.28 Å), and the lone pair are nearly coplanar. The second (axial) S is part of a 57.8° S–Te–S bond angle with the two S atoms separated by 2.98 Å. Such a pseudorotation, but in the reverse direction, has been suggested for the oxidative addition of



Figure 7. Tellurorhodamine structures in the reaction pathway for reduction of telluroxide 2 to tellurorhodamine 1 with methanethiol. Energies are relative to 1 in the balanced reaction and follow from Figure 6. The inset shows changes in geometry around the Te atom in the progression from E (left) to  $TS_E$  (center) to 1 (right).





bromine to diorganoselenides and tellurides.<sup>40</sup> As the reaction progresses through the transition state, the disulfide is produced (S–S bond length of 2.09 Å) via reductive elimination regenerating **1** with a Te(II) center.

#### CONCLUSIONS

Catalytic amounts of tellurorhodamine 1 were used to oxidize aromatic thiols to disulfides under aerobic conditions with visible-light irradiation. Catalytic amounts of selenorhodamine 3 with visible-light irradiation gave slower and/or poorer oxidation of thiols to disulfides. While both 1 and 3 produce  ${}^{1}O_{2}$  efficiently upon irradiation, the self-sensitized generation of  ${}^{1}O_{2}$  upon irradiation of 1 leads to oxidation of 1 to telluroxide 2, which is the true oxidant for the conversion of thiols to disulfides. Selenorhodamine 3 does not form the corresponding selenoxide intermediate under the conditions of the reaction, and disulfide production is likely from the generation and subsequent reaction of  ${}^{1}O_{2}$ .

The overall photocatalytic pathway is summarized in Scheme 4. Two equivalents of the telluroxide 2 can be formed from pertelluroxide A reacting with a second molecule of A. We propose a second pathway that also produces telluroxide 2. Formation of a hydroxy(perhydroxy)tellurane from the reaction of 1 with  ${}^{1}O_{2}$  and water (structure **B** in Scheme 4) is followed by loss of  $H_2O_2$  to give telluroxide 2. Telluroxide 2 oxidizes two thiol molecules via sequential addition of thiols to generate first intermediates D and then intermediate E plus a molecule of water. Reductive elimination of disulfide from intermediate E regenerates tellurorhodamine 1, which reenters the photocatalytic cycle. By analogy to telluride catalysts for the activation of  $H_2O_2$ <sup>15,16,39</sup> tellurorhodamine 1 (the telluride state) is the resting form of the catalyst and tellurorhodamine telluroxide 2 is the active form of the catalyst. This mechanistic analysis is supported experimentally and computationally.

#### EXPERIMENTAL SECTION

**Preparation of 3,6-Bis(dimethylamino)-9-(2,4,6-trimethylphenyl)-9H-telluroxanthen-9-ylium Hexafluorophosphate** (1).<sup>11</sup> Tellurorhodamine 1 was prepared by the addition of the Grignard reagent prepared from 2-bromomesitylene to 3,6-bis(dimethylamino)-9H-telluroxanthen-9-one (4)<sup>20</sup> as described in ref 11. Dye 1 was isolated in 80% yield, and its spectroscopic properties were identical with those reported for 1 in ref 11: mp >260 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.52 (d, 1 H, J = 3.0 Hz), 7.51 (d, 1 H, J = 10.0 Hz), 7.06 (s, 2 H), 6.76 (d × d, 2 H, J = 3.0, 10.0 Hz), 3.21 (s, 12 H), 2.42 (s, 3 H), 1.83 (s, 6 H);  $\lambda_{max}$  in MeOH ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 600 nm (8.6 × 10<sup>4</sup>).

Preparation of 3.6-Bis(dimethylamino)-9-(2.4.6-trimethylphenyl)-9H-selenoxanthen-9-ylium Hexafluorophosphate (3). 2-Bromomesitylene (0.86 g, 4.3 mmol) was added to a stirred suspension of magnesium ( $\bar{0}.12$  g, 4.8 mmol) in anhydrous THF (2 mL). The mixture was stirred at ambient temperature for 3 h, and the resulting Grignard solution was transferred via cannula to a stirred suspension of 3,6-bis(dimethylamino)-9H-selenoxanthen-9-one (5;<sup>2</sup> 0.10 g, 0.29 mmol) in anhydrous THF (8 mL). The resulting mixture was heated at reflux for 24 h, cooled to ambient temperature, and quenched by the addition of glacial acetic acid (1 mL). The resulting mixture was poured into 50 mL of 10% (by weight) aqueous HPF<sub>6</sub>. After 12 h, the resulting precipitate was collected via filtration and washed with water (10 mL) and diethyl ether ( $4 \times 10$  mL) to give 0.11 g (62%) of 3 as a green solid: mp 175–177 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, 2 H, J = 10.0 Hz), 7.34 (d, 2 H, J = 2.0 Hz), 7.04 (s, 2 H), 6.81 (d × d, 2 H, J = 2.0, 10.0 Hz), 3.28 (s, 12 H), 2.42 (s, 3 H), 1.83 (s, 6 H); <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 163.2, 153.7, 146.2, 139.6, 137.4, 135.9, 133.5, 129.0, 119.7, 115.8, 109.1, 40.9, 21.3, 19.7;  $\lambda_{max}$  in MeOH ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 568 nm (1.03 × 10<sup>5</sup>);  $\lambda_{max}$  in CH<sub>2</sub>Cl<sub>2</sub> ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 567 nm (7.76 × 10<sup>4</sup>); HRMS (ESI) m/z449.1518 (calcd for  $C_{26}H_{29}N_2^{80}Se^+$  449.1490). Anal. Calcd for C26H29N2Se•PF6: C, 52.62; H, 4.93; N, 4.72. Found: C, 52.41; H, 5.05; N, 4.65.

**Photooxidation of 1.** In Aqueous MeOH. A solution of 1 (1 ×  $10^{-5}$  M) in 90% MeOH/10% water was irradiated with white LEDs and monitored by UV–vis absorption every 2 min to give the spectra shown in Figure 2a. From this photooxidized sample, the H<sub>2</sub>O<sub>2</sub> concentration was determined spectrophotometrically.<sup>26</sup> A stock solution of oxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]titanium(IV) (5 ×  $10^{-6}$  M) in perchloric acid (2 M) was prepared. Aliquots ( $10 \,\mu$ L) of the photooxidized sample were added to 3 mL of the stock solution, and the change in absorption at 432 nm was used to determine the H<sub>2</sub>O<sub>2</sub> concentration by comparing to a reference of an aliquot ( $10 \,\mu$ L) of an aqueous urea peroxide solution ( $1.0 \times 10^{-5}$  M). The samples were referenced to a blank using water ( $10 \,\mu$ L). The analysis was run in triplicate, and the concentration of H<sub>2</sub>O<sub>2</sub> was

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determined to be (8.4  $\pm$  0.6)  $\times$  10^{-6} M (0.84 equiv in comparison to 1).

In Aqueous Chloroform after Thiophenol Oxidation. A solution of 1 ( $5 \times 10^{-4}$  M) and thiophenol ( $5 \times 10^{-2}$  M) in chloroform (2 mL) and water ( $50 \ \mu$ L) was irradiated with white LEDs. Upon a visual change in color, from a blue to a green solution, water (2 mL) was added to create a biphasic solution. From the aqueous layer an aliquot ( $10 \ \mu$ L) was used to determine the H<sub>2</sub>O<sub>2</sub> concentration using oxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]titanium(IV) as described above. The concentration of H<sub>2</sub>O<sub>2</sub> was determined from triplicate runs and was ( $1.8 \pm 0.1$ )  $\times 10^{-6}$  M (0.36 equiv in comparison to 1).

**Photocatalytic Thiol Oxidation.** Stock solutions of thiophenol, 2-naphthalenethiol, 2,6-dichlorothiophenol, *tert*-butyl mercaptan, and dodecanethiol  $(1 \times 10^{-1} \text{ M})$  were prepared in 1 mL of CDCl<sub>3</sub>. A stock solution of  $\mathbf{1}$   $(1 \times 10^{-3} \text{ M})$  or  $\mathbf{3}$   $(1 \times 10^{-3} \text{ M})$  was prepared in 2 mL of CDCl<sub>3</sub> with cyclohexane added as an internal standard. A 0.2 mL portion of the stock solution of  $\mathbf{1}$  or  $\mathbf{3}$  and 0.2 mL of one of the thiol stock solutions were mixed in 5 mm NMR tubes, resulting in a final concentration of  $5 \times 10^{-2}$  M of thiol and  $5 \times 10^{-4}$  M of  $\mathbf{1}$  or  $\mathbf{3}$  for each sample. A 10  $\mu$ L aliquot of water was added to each NMR tube. The samples were irradiated by 24 W white LEDs with magnetic stirring (using a straightened paperclip sealed in a glass capillary), and the <sup>1</sup>H NMR spectrum was taken every 20 min.

**Reduction of 2 to 1 by Aromatic Thiols.** A solution of 2 (1 ×  $10^{-5}$  M) was prepared by dissolving 1 in 95% MeOH and oxidizing the solution with self-sensitized generation of  ${}^{1}O_{2}$ . The reduction of 2 to 1 with sequential additions of 0.5 equiv of thiophenol, 2-naphthalenethiol, or 2,6-dichlorothiophenol was followed by UV–vis absorption spectroscopy. The addition of 2 equiv of thiol gave complete reduction of 2 to 1 (Supporting Information).

**Stopped-Flow Experiments.** Stock solutions of thiophenol, 2-naphthalenethiol, 2,6-dichlorothiophenol, and dodecanethiol ( $5 \times 10^{-4}$  M) were prepared in 99% MeOH. A stock solution of 2 ( $5 \times 10^{-6}$  M) in 99% MeOH was used for each scan. The rate of the consumption of 2 was monitored at 655 nm for each thiol. The acquired scans from mixing equal volumes of the stock solutions of 2 and thiol are shown as an average of triplicate measurements in Figure 4. The sample-handling unit was fitted with two drive syringes that were mounted inside a thermostated-bath compartment, which allowed for variable-temperature experimentation. The optical detection cell was set up in the 10 mm path length.

**Determination of Singlet Oxygen Yield for Selenorhodamine 3.** Generation of  ${}^{1}O_{2}$  was assessed by its luminescence peak at 1270 nm. Time-resolved detection of the long-lived  ${}^{1}O_{2}$  emission was used to distinguish the signal from  ${}^{1}O_{2}$  as previously described.<sup>11</sup> The samples (MeOH solutions of **3** or tetramethylselenorosamine used as a standard in quartz cuvettes) were placed in front of the spectrometer entrance slit.

**Computational Details.** Calculations were done with Gaussian09<sup>28</sup> input files, and results were visualized using GaussView05.<sup>41</sup> All structures were optimized using the B3LYP<sup>29,31</sup> level of theory with the 6-31+G(d)<sup>32-34</sup> basis set for all light atoms and LanL2DZ<sup>35-37</sup> for Te. Transition states were located with the QST2 keyword. Energy values were obtained from the free energy from the frequency calculations. The HOMO and LUMO of the reduced tellurorhod-amine 1 and the oxidized tellurorhodamine telluroxide 2 were obtained from the optimized structures.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00166.

General methods, NMR spectral data for 1 and 3, elemental analysis of 3, the spectrum of the LED light source, photos of the observed color change of 1 and 2,

titration of 2 with various thiols, and calculated total energies (PDF)

Cartesian coordinates of the calculated structures (XYZ)

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This research was supported in part by the National Science Foundation (CHE-1566142). T.M.M. thanks Portland State University for financial support and Prof. R. Simoyi for use of the stopped-flow spectrometer.

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